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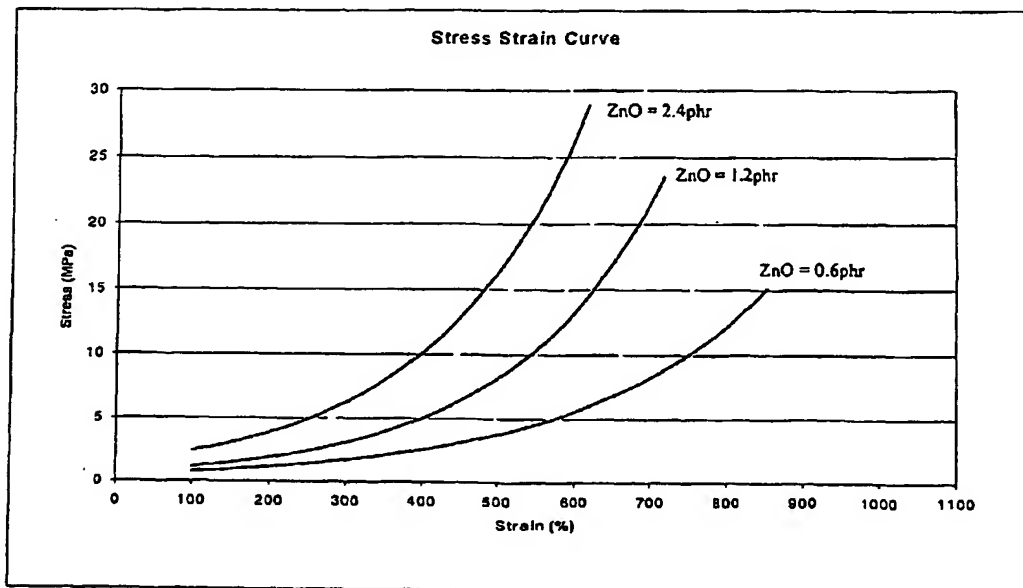
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(54) Title: A SYNTHETIC LATEX COMPOSITION



(57) Abstract: There is provided a synthetic latex compound composition for producing non-staining dipped rubber articles such as a non-staining glove, condom, finger cot and balloon, comprising of a synthetic carboxylated acrylonitrile butadiene rubber or a synthetic carboxylated butadiene co-polymer rubber, free from any sulphur or sulphur containing chemicals or accelerators. The sole cross-linking system comprising only of polyvalent metal chemicals, rendering the rubber articles, free from copper staining or staining with other heavy metals, as well as being free from Type I and Type IV Allergens.

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## A SYNTHETIC LATEX COMPOSITION

### FIELD OF THE INVENTION

The present invention relates to novel types of synthetic latex composition, which are identified as being suitable for producing non-staining dipped rubber articles such as a non-staining glove, condom, finger cot and balloon. More particularly, the invention relates to synthetic latex compositions, using synthetic carboxylated butadiene co-polymer latex containing only polyvalent metal chemical(s) for cross-linking, to produce non-staining rubber gloves. The stains, which are usually brown in colour, are usually observed when typical synthetic and natural rubber gloves are worn for as little as a few minutes. Also, the compositions described herein render the rubber articles, which are free from known allergens, which would normally cause allergic response in some individuals. The applicable synthetic elastomer latices are synthetic carboxylated polymer latices, such as carboxylated acrylonitrile butadiene latex, carboxylated acrylic butadiene latex, carboxylated styrene butadiene latex, carboxylated chloro-butadiene latex or other carboxylated latex co-polymers of butadiene, which may be cross-linked, only using polyvalent metal chemicals, without the use of sulphur, sulphur containing accelerators, formaldehyde or unsaturated cross-linkable monomers.

### BACKGROUND ART

Over the last two decades, the use of rubber gloves has increased to enormous numbers, arising for the need to protect individuals from highly contagious and dangerous transmittable diseases. However, along with this increasing use of rubber gloves, the market has become aware of some of the adverse reactions,

both physiological and aesthetic, to the wearing or contact with such gloves. The physiological reactions are caused by allergic response to the rubbers or chemical constituents of the rubber formulation. The most publicised allergic reaction is that caused by contact by sensitised individuals with latex protein allergens, which are present in natural rubber latex and which, in severe cases of reaction, can lead to anaphylactic shock. This is known as Type I Allergy. This problem has resulted in a growing market for synthetic gloves, which should be free from protein allergens, provided the manufacturer takes precautions to ensure there is no cross-contamination with latex rubber products and the machinery processing the latter.

The second, more common allergic reaction, Type IV, is a contact reaction, caused by chemicals in the rubber, which can give rise to unpleasant skin reactions such as dermatitis. The other, aesthetic problem, "copper staining" is very common, with all conventionally sulphur vulcanised natural and synthetic rubbers. It manifests itself by the gradual appearance of brown stains on the gloves, which give the effect of being soiled.

The ability to produce cross-linking within carboxylated synthetic polymers, using polyvalent metal oxides, polyvalent metal hydroxides, polyvalent metal salts (inorganic and organic) and polyvalent metal complexes has been well established. The cross-linking occurs by reaction of the polyvalent metal cation with two or more carboxylic anions which are present as part of the chemical structure of the elastomeric polymer chain.

US Patent No. 2,662,874 discloses preparation of carboxyl containing polymers, which may be subsequently cross-linked by milling solid carboxylated polymer with polyvalent metal oxides such as those of zinc, magnesium, calcium, cadmium, titanium, aluminium, barium, strontium, copper, cobalt, tin, iron, lead  
5 and others, to produce dry rubber compounds. This patent reports similar results with polyvalent metal hydroxides, which are essentially hydrated oxides.

UK Patent No. 785,631 discloses a process for the production of shaped articles from elastomeric polymers containing reactive groups. Included in this  
10 group of reactive polymers are polymers containing carboxyl groups, carbonyl groups, sulphonic acid groups, amide or basic groups, which may react with water-soluble salts or hydroxides of polyvalent metals, such as calcium chloride, barium chloride, magnesium chloride, zinc chloride, zinc sulphate, ferrous sulphate, barium hydroxide, calcium hydroxide, chromium acetate, chrome  
15 alum, copper acetate and aluminium salts. The process involves introducing the reactive polymer into a coagulant bath, which contains water-soluble salts or hydroxides of polyvalent metals and thereafter, moulding or extruding articles from the coagulated product.

UK Patent No. 862,372 discloses the invention of aqueous dispersions of  
20 carboxyl containing elastomers, which, in the presence of formaldehyde, are able to utilise cross-linkers such as oxides, hydroxides and carbonates of zinc, magnesium and calcium. Such compositions were said to be suitable to produce crack-free films for articles such as gloves, but that the presence of formaldehyde was necessary.

US Patent No. 3,403,136 discloses the use of a cross-linking system for solid carboxylic elastomers, comprising of polyvalent metal oxides, combined with their corresponding peroxides, which prevents pre-cure of the polymer. The preferred peroxides and oxides were those of Group II of the Periodic Table, in particular zinc, calcium and magnesium. This patent pertains to dry rubber compounds.

US Patent No. 3,976,723 discloses processes in which carboxyl containing acrylic polymers, in the solid form, are mixed with polyvalent metallic oxides in a mill or internal mixer prior to curing. The polyvalent metallic oxides include those of zinc, magnesium, cadmium, calcium, titanium, aluminium, barium, strontium, copper, cobalt, tin and others, as well as polyvalent metallic hydroxides.

Japanese Patent No. 61-278546 discloses the use of metal oxides or hydroxides of zinc or magnesium for the cross-linking of carboxylated chloroprene rubber latex, used for foam rubber.

US Patent No. 4,525,517 discloses the use of one or more polyvalent metal oxides and one or more alkali metal salts (lithium, sodium or potassium) salts of C<sub>12</sub>-18 alkanolic acids, to mill with solid carboxylated nitrile rubber, so as to produce vulcanisable dry rubber compositions with improved scorch resistance.

US Patent No. 5,014,362 discloses an elastomeric material to produce gloves having the ability to relax after initial stretching, such that the pressure on the hand is reduced. It describes the preferred material comprising a carboxylated nitrile butadiene rubber and containing a metallic compound, preferably oxides

of lead, magnesium and zinc. The preferred oxide is zinc oxide, claimed at levels from 0.1 to 0.5 parts per 100 parts (phr) of nitrile butadiene rubber. Example formulations in this patent also contain higher levels of sulphur (1.0 phr) and zinc dibutyl dithiocarbamate (1.0phr).

5

All the manufacturers of commercially available carboxylated acrylonitrile butadiene latex (nitrile latex) describe the two cross-linking mechanisms which are said to function with their materials. One mechanism is via sulphur cross-linking between the diene sections of molecules of the polymer and the other cross-links are due to ionic bonding formed by reaction between carboxyl groups in the nitrile polymer and metal oxides. Consequently, all the manufacturers of nitrile latex provide guideline formulations, which contain both sulphur and thio accelerators, together with zinc oxide.

## 15 SUMMARY OF THE INVENTION

Accordingly there is provided a process for preparing a synthetic latex compound, the said process includes the steps of a) adding a polyvalent metal chemical or a mixture thereof, to a surfactant stabilised synthetic carboxylated latex, or blend with other synthetic latex, to form a synthetic latex compound, b) stirring the synthetic latex compound, c) diluting the synthetic latex compound obtained in step (b) to a predetermined total solid content (TSC) and d) maintaining the synthetic latex compound obtained in step (c) at a temperature between 0 to 80°C.

25 Further, there is also provided a synthetic latex compound obtained from a process which includes the steps of a) adding a polyvalent metal chemical or a

mixture thereof to a surfactant stabilised synthetic carboxylated latex, or blend with other synthetic carboxylated or non-carboxylated latex or latices to form a synthetic latex compound, b) stirring the synthetic latex compound, c) diluting the synthetic latex compound obtained in step (b) to a predetermined total solid content (TSC) and d) maintaining the synthetic latex compound obtained in step (c) at a temperature between 0 to 80°C.

Also provided non-staining dipped rubber articles such as a non-staining glove, condom, finger cot or balloon made from composition containing an effective amount of synthetic carboxylated butadiene co-polymer latex and an effective amount of polyvalent metal chemical or mixture thereof as the sole cross-linking agent.

And, there is also provided non-staining dipped rubber articles such as a non-staining rubber article such as glove, condom, finger cot or balloon made from a composition containing an effective amount of synthetic polymer latex or latices, an effective amount of synthetic carboxylated butadiene co-polymer latex and an effective amount of polyvalent metal chemical as the sole cross-linking agent.

20

The present invention consists of certain novel features and a combination of parts hereinafter fully described and illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the scope of the invention, or sacrificing any of the advantage of the present invention.



## **BRIEF DESCRIPTION OF THE DRAWINGS**

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings the preferred embodiments thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

Figure 1 shows the effect of the level of zinc oxide on the tensile properties of gloves, using a commercially available carboxylated nitrile latex.

10

Figure 2 shows the different physical properties attained when using a number of commercially available carboxylated nitrile latices, from different manufacturers, using the same base formulation.

15 Figure 3 shows a flow diagram, which shows the typical manufacturing processes for the production of dipped rubber articles such as gloves.

## **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

20 The present invention relates to processes for producing non-staining dipped rubber articles such as a non-staining glove, condom, finger cot and balloon from synthetic latex and a latex composition for producing the same. More particularly, the invention relates to processes for producing a non-staining glove made from synthetic elastomeric compositions, which are free from the  
25 common problem of unsightly brown stains, which are usually observed when typical synthetic and natural rubber gloves are worn for as little as a few

minutes and a novel synthetic latex composition for producing non-staining rubber articles such as a non-staining glove, condom, finger cot and balloon. Hereinafter, this specification will describe the processes for producing a non-staining glove from synthetic carboxylated latex compound according to the preferred embodiments and by referring to the accompanying drawings and the latex compound. However, it is to be understood that limiting the description to the glove and to the preferred embodiment of the invention and with reference to the accompanying drawings is merely to facilitate discussion of the present invention and it is envisioned that those skilled in the art may devise various modifications and equivalents without departing from the scope of the appended claims.

The invention as described hereinafter, describes processes for producing non-staining gloves, which are free from some if not all of the above-mentioned problems. The gloves may be produced from carboxylated synthetic copolymers of butadiene, including carboxylated acrylonitrile butadiene latex, carboxylated acrylic butadiene latex, carboxylated chloroprene latex and other carboxylated synthetic polymers. The preferred synthetic latex is carboxylated acrylonitrile butadiene latex and the inventors have evaluated most of the nitrile latices available commercially. The inventors have established that this technology can be applied to all, but their evaluations have shown that all nitrile latices, even those having the similar levels of acrylonitrile/butadiene/carboxylic acid levels, can exhibit markedly different physical properties in the same formulation.

The sole cross-linking mechanism employed utilises ionic bonding between polyvalent metal ions and the carboxylate groups of the elastomer. The preferred sources of polyvalent metal ions are zinc oxide, zinc carbonate and calcium carbonate or any combinations of these, although the inventors have

5 established that other sources such as magnesium oxide, magnesium carbonate, hydroxides of calcium, magnesium, aluminium and also aluminates, can be effective to give sufficient cross-linking. In the case of zinc oxide, it has established that levels from 0.6 to 2.5phr are able to give sufficient cross-linking to meet the physical requirements for use in medical gloves. It has been further

10 established that formulations utilising a synergistic combination of zinc oxide and polyvalent metal carbonates e.g. ultra-fine calcium carbonate, which are capable of producing gloves, which easily meet today's rigorous standards.

The process employed in the production of gloves, utilising this technology is

15 the typical process used in current manufacture of unsupported gloves of thickness, typically 0.1 to 0.2 mm thick. The latex compound is produced in conventional latex compounding mixing tanks, by adding pre-dispersed zinc oxide or other source of polyvalent metal, to a surfactant stabilised synthetic carboxylated latex, such as nitrile latex. The latex compound would normally be

20 stirred for several hours and then diluted to the normal TSC required for a particular glove dipping line. The normal TSC would be in the range 25 to 35% and the latex would be maintained at a temperature of about 25°C.

The dipping process used is that of a coagulant dipping process and the

25 coagulant normally used is aqueous or aqueous/alcohol solutions of calcium nitrate, calcium chloride or mixture of the two, at concentrations from 10% to

30%. Depending on the process requirements, a suitable mould release additive (in the case of powder-free coagulants), plus a suitable wetting agent would be used, while a powder coagulant may be used for powdered gloves. After dipping in the coagulant, the glove formers are dried at temperatures in the range 70 to 100°C and then cooled to about 50°C. The formers then dip into the latex compound and, after partial drying, the latex-coated formers are leached in water at about 45°C. The gloves may then be further processed by different methods, and three examples are given.

In the case of on-line polymer coated gloves, the gloves on the formers would then be dipped into a selected polymer dispersion, followed by beading. The formers would then enter the cure/drying oven, where the films are subjected to temperatures 100 to 120°C for up to 40 minutes. This is followed by leaching in water at about 70°C, dried at about 100°C and finally cooled before stripping the polymer coated gloves from the formers. In the case of on-line chlorination, the gloves would be beaded after the pre-cure leach, then cured as above. This would then be followed by an on-line chlorination process, leaching, drying and finally, cooling before stripping.

The third option would be to utilise a powder coagulant system followed by a powder slurry after curing and then process the gloves off-line, either by chlorination or a suitable anti-tack process for powder-free gloves. If powdered gloves are required, there is no need for any off-line processing.

The invention as described hereinafter relates to the development of simple formulations, using only polyvalent metal chemicals as the sole system for

cross-linking synthetic carboxylated butadiene co-polymer type elastomers, to produce articles such as gloves, which are non-staining and possess the required tensile properties for medical gloves. It is commonly considered that sulphur and sulphur containing accelerators are essential in combination with

5 polyvalent metal chemicals to compound with synthetic carboxylated butadiene co-polymer type latices in order to produce rubber articles such as gloves, which meet the tensile properties for various worldwide regulatory organisations such as ASTM and EN.

10 Also, the formulations described in this invention do not contain any cross-linkable monomers, which could also be utilised to make non-staining rubber articles. The staining referred to, is usually readily observed when the typical synthetic and natural rubber gloves are worn for as little as a few minutes. It is due to reaction between the sulphur-containing chemicals used as accelerators

15 and traces of metals such as copper, silver, lead, nickel or other reactive metals, when the wearers hands contact objects such as coins, keys, handles, etc.

The said latex compound is prepared in conventional latex compound mixing

20 tanks. The polyvalent metal chemical or chemicals are normally added in a liquid form, either as an aqueous dispersion or aqueous solution to a surfactant stabilised synthetic carboxylated latex in a stirred mixing tank. Other materials are normally added, such as alkali, for pH adjustment and pigment, for a desired colour. The latex compound is then normally diluted with demineralised

25 water to attain a desired Total Solids Content (TSC) and the stirred compound is usually maintained at a temperature in the range 20 to 30°C, although

temperatures up to 80°C or as low as 0°C may be used. After stirring at low speed to facilitate complete de-aeration, the latex compound may be transferred to the latex dip tank on a conventional dipping machine for dipped rubber goods.

5

Figure 1 shows the effect of the level of zinc oxide on the tensile properties of gloves, using a commercially available carboxylated nitrile latex. It shows clearly that the tensile strength increases steadily, with increased levels of zinc oxide, together with increase in 300% modulus and a steady decrease in Elongation at

10 Break (shown as the end of each curve).

Figure 2 demonstrates the different physical properties attained when using a number of commercially available carboxylated nitrile latices, from different manufacturers, using same base formulation. However, as mentioned earlier, it

15 is possible to attain the desired physical properties by adjustments to the formulation for each type of synthetic carboxylated latex.

Figure 3 illustrates the typical manufacturing processes for the production of dipped rubber articles, in particular, rubber gloves. The process includes the

20 steps of:

- a) starting at the "former cleaning" stage, where the rubber article formers are cleaned by immersion in cleaning fluids, combined with mechanical brushing,
- b) the clean formers are dried in an oven at temperatures in the range 70 to
- 25 100°C,
- c) the formers are cooled to a temperature in the range 50 to 70°C,

- d) the formers may either dip into a powder coagulant (Path 1), or into a powder-free coagulant (Path 2). The coagulant normally contains an aqueous, aqueous/alcohol or alcohol solution of a calcium salt plus wetting agent and powder or a powder-free material as a "release agent",
- 5 e) the coagulant coated former is dried in an oven at a temperature in the range 70 to 100°C,
- f) the coagulant coated former is cooled to a temperature of 40 to 60°C,
- g) the coagulant coated former is dipped into the latex compound which is maintained at a temperature in the range 20 to 30°C,
- 10 h) the latex compound coating on the former is then partially dried at a temperature in the range 30 to 70°C,
- i) the partially dried film on the former is leached in water or an aqueous solution at a temperature in the range 30 to 50°C,
- j) the leached film on the former may then dip into a polymer dispersion
- 15 (Path 3) or by-pass the polymer tank (Path 4),
- k) the rubber article is beaded,
- l) the rubber article on the former is then cured in an oven at a temperature in the range 80 to 120°C,
- m) the cured rubber article on the former then passes either into a post-cure
- 20 leaching process containing water or an aqueous solution at a temperature in the range 50 to 80°C (Path 5) or
- n) into an on-line chlorination process (Path 6),
- o) for post-cure leached rubber articles, they may dip into a powder slurry (Path 7) or by-pass the slurry (Path 8) for gloves from (j), which have
- 25 been polymer coated as Path 3,

p) the rubber articles on the formers from either (n) or (o) are then dried at a temperature in the range 80 to 100°C, and

q) the dried rubber articles are stripped from the formers.

- 5 Rubber articles from the various flow paths described above may be used to make various versions of rubber articles. In the case of rubber gloves, the options are powdered gloves, off-line chlorinated gloves, off-line anti-tack processed gloves, outer powdered/inner polymer-coated gloves, off-line chlorinated/polymer coated powder-free gloves, off-line processed polymer-
- 10 coated powder-free gloves, outer powdered/inner on-line chlorinated gloves, outer powder-free/inner on-line chlorinated powder-free gloves, off-line chlorinated/on-line chlorinated powder-free gloves, off-line anti-tack/on-line chlorinated powder-free gloves and powder-free polymer-coated gloves.
- 15 For powdered gloves, the manufacturing process, from the flow diagram follows Paths 1, 4, 5 and 7 and then the gloves are dried, cooled and packed. For off-line chlorinated gloves, the powdered gloves are processed in an off-line chlorinator, dried, cooled and packed. For off-line anti-tack processed gloves, the powdered gloves are processed in a machine using an anti-tack additive,
- 20 dried, cooled and packed. For outer powdered/inner polymer-coated gloves, the manufacturing process, from the flow diagram follows Paths 1, 3, 5 and 8 and then the gloves are dried, cooled and packed. For off-line chlorinated/polymer coated powder-free gloves, the outer powdered/inner polymer-coated gloves are processed in an off-line chlorinator, dried, cooled and packed. For off-line
- 25 processed polymer-coated powder-free gloves, the outer powdered/inner polymer-coated gloves are processed in a machine using an anti-tack additive,



dried, cooled and packed. For outer powdered/inner on-line chlorinated gloves, the manufacturing process, from the flow diagram follows Paths 1, 4, and 6 and then the gloves are dried, cooled and packed. For outer powder-free/inner on-line chlorinated powder-free gloves, the manufacturing process, from the flow diagram follows Paths 2, 4 and 6 then dried, cooled and packed. For off-line chlorinated/on-line chlorinated powder-free gloves, the outer powdered/inner on-line chlorinated gloves are subjected to an off-line chlorination process in order to chlorinate the outer surface of the gloves and then the gloves are dried, cooled and packed. For off-line anti-tack/on-line chlorinated powder-free gloves, the outer powdered/inner on-line chlorinated gloves are processed in a machine using an anti-tack additive, dried, cooled and packed. For powder-free polymer-coated gloves, the manufacturing process, from the flow diagram, follows Paths 2, 3, 5 and 8 and then the gloves are dried, cooled and packed. These gloves may also be further processed off-line for enhanced surface properties.

For the purpose of this specification, one commercially available carboxylated nitrile latex was selected, compounded to a formulation (as shown in Table 1) and processed to produce powder-free nitrile gloves, free from known allergens and staining, with a tensile strength at break of 18 to 20 Mpa, a 300% Modulus of less than 2.0 Mpa and Elongation at break in excess of 750%. The same films show minimal change in these tensile properties after ageing for 7 days at 70°C, as shown in the data in Table 2.

**TABLE 1**

MATERIAL	QUANTITY (phr)
Nitrile latex	100.00
Stabiliser	0.50
Polyvalent metal oxide	1.20
Antioxidant	0.50
Anti-tack agent	1.00

**TABLE 2**

5 Properties of a typical non-staining powder-free nitrile glove.

PROPERTY	RESULT	
	Un-aged	Aged at 70°C for 7 days
Tensile strength (Mpa)	19	20
300% modulus (Mpa)	1.8	1.9
500% modulus (Mpa)	3.1	3.4
Elongation at Break (%)	800	800

Attention has been given to relaxation properties, in order to understand what factors affect the relaxation properties of films such as carboxylated nitrile rubber. US Patent 5,014,362 describes an invention that gloves can be produced, with a carboxylated nitrile latex, using levels of zinc oxide from 0.1 to 0.5 phr, combined with sulphur and a dithiocarbamate, to give films possessing special relaxation properties. The invention claims that such formulations can

give rise to processed films which, after initial stretching of 100%, the stress can fall off to less than 10% of original stress after 6 minutes, while maintaining an elongation of 100%.

- 5 The present inventors' evaluations on formulations containing levels of zinc oxide up to 2.5 phr were conducted using different sources of nitrile latex and the relaxation properties were such that all retained less than 10% of original stress after 6 minutes at 100% elongation. In addition to this, relaxation studies were conducted on a number of different nitrile latex films, without the presence
- 10 of cross-linking agents such as polyvalent metal chemicals, sulphur vulcanisation chemicals or reactive monomers, which were dipped by multiple "straight dips", to avoid any cross-linking by the polyvalent metal calcium ions of the coagulant system. These films were subjected to stretching to 100% to measure relaxation properties and the relaxation properties were also found to
- 15 be the same as those above. It was found that a new commercial carboxylated nitrile latex could be compounded using a conventional cure formulation with 0.5 phr of zinc oxide, 1.0 phr of zinc dibutyl dithiocarbamate and 1.0 phr of sulphur. This latter material exhibited relaxation properties, which did not relax in the same manner, but was intermediate between the relaxation properties of
- 20 natural rubber and those of other nitrile rubber latex.

From these studies, it can be concluded that the relaxation properties of films dipped from carboxylated nitrile latex, appear to be an intrinsic property of any particular latex, rather than the nitrile latex compound formulation.

- 25 The following are examples of formulations and process conditions, but are not intended to be limiting.

**EXAMPLE 1**

A carboxylated nitrile latex was compounded with various additives as in Table  
5 3 below.

**TABLE 3**

MATERIAL	QUANTITY (phr)
Nitrile latex	100.00
Stabiliser	0.50
Polyvalent metal oxide	0.60
Antioxidant	0.50
Polyvalent metal carbonate	5.00
Anti-tack agent	1.00

The above formulation was stirred gently overnight and the total solids content  
adjusted to 30%. Formers were cleaned on-line, using propriety cleaning  
10 chemicals, which after passing through a rinse water tank, were dried in an  
oven at about 80°C. The formers then dipped into a coagulant containing 25%  
calcium nitrate and a stearate-based release agent. The coagulant coated  
formers were then dried at a temperature in the range 70 to 100°C, followed by  
cooling to about 50°C. The coagulant coated formers were then dipped into the  
15 latex compound with a dwell time of 10 seconds. The latex compound coated  
formers then passed through a gelling oven at 60°C, followed by leaching in  
water at 45°C for 2 minutes and then beading. The gloves on the formers were  
then cured/dried in an oven with temperatures up to 120°C for 30 minutes. The  
emerging gloves were cooled in a water bath and then entered an on-line

chlorination process, followed by final drying, cooling and stripping. Table 4 shows typical properties of the gloves from this process.

**TABLE 4**

5 Typical properties of on-line chlorinated powder-free non-staining nitrile gloves.

PROPERTY	RESULT	
	Un-aged	Aged at 70°C for 7days
Tensile strength (Mpa)	22	20
300% modulus (Mpa)	1.8	1.7
500% modulus (Mpa)	3.4	3.2
Elongation at Break (%)	800	800

**EXAMPLE 2**

A carboxylated acrylic butadiene co-polymer latex was compounded with  
10 various additives as in Table 5 below.

**TABLE 5**

MATERIAL	QUANTITY (phr)
Carboxylated acrylic butadiene co-polymer Latex	100.00
Stabiliser	0.50
Polyvalent metal oxide	2.00
Antioxidant	0.50
Polyvalent metal carbonate	5.00
Anti-tack agent	1.00

The above formulation was stirred gently overnight and the TSC adjusted to 30%. Formers were cleaned on-line, using propriety cleaning chemicals, which after passing through a rinse water tank, were dried in an oven at about 80°C. The formers then dipped into a coagulant containing 25% calcium nitrate and a

5    stearate-based release agent at about 55°C. After cooling, the coagulant coated formers were dipped in the latex compound, with a dwell time of 10 seconds. The formers then passed through a gelling oven at 60°C, followed by leaching in water at 45°C for 2 minutes and then beading. The gloves were cured/dried in an oven with temperatures up to 120°C for 30 minutes. The emerging gloves

10    were cooled in a water bath and then entered an on-line chlorination process, followed by final drying, cooling and stripping. Table 6 shows typical properties of the gloves from this process.

**TABLE 6**

15    Typical properties of on-line chlorinated powder-free non-staining acrylic-butadiene polymer-based gloves.

PROPERTY	RESULT	
	Un-aged	Aged at 70°C for 7days
Tensile strength (Mpa)	16	27
300% modulus (Mpa)	3.3	4.1
500% modulus (Mpa)	6.5	9.6
Elongation at break (%)	750	700

**EXAMPLE 3**

A blend of a carboxylated nitrile latex and synthetic chloroprene latex was compounded with various additives as in Table 7 below.

**5 TABLE 7**

MATERIAL	QUANTITY (phr)
Nitrile latex	90.00
Synthetic chloroprene latex	10.00
Stabiliser	0.50
Polyvalent metal oxide	2.40
Antioxidant	0.50
Polyvalent metal carbonate	5.00
Anti-tack agent	1.00

The above formulation was stirred gently overnight and the TSC adjusted to 30%. Formers were cleaned on-line, using propriety cleaning chemicals, which after passing through a rinse water tank, were dried in an oven at about 80°C.

- 10 The formers were dipped into a coagulant containing 25% calcium nitrate and a stearate-based release agent at 55°C. After cooling, the coagulant coated formers were dipped in the latex compound, with a dwell time of 10 seconds. The latex compound coated formers then passed through a gelling oven at 60°C, followed by leaching in water at 45°C for 2 minutes and then beading.
- 15 The gloves on the formers were then cure/dried in an oven with temperatures up to 120°C for 30 minutes. The emerging gloves on the formers were cooled in a water bath and then entered an on-line chlorination process, followed by final

drying, cooling and stripping. Table 8 shows typical properties of the gloves from this process.

**TABLE 8**

- 5 Typical properties of on-line chlorinated powder-free non-staining gloves made using a compound based on a blend of nitrile and chloroprene latices.

PROPERTY	RESULT	
	Un-aged	Aged at 70°C for 7days
Tensile strength (Mpa)	21	25
300% modulus (Mpa)	2.7	2.8
500% modulus (Mpa)	5.5	6.1
Elongation at Break (%)	750	750

- 10 Tests to demonstrate the non-staining properties were conducted by immersing gloves in aqueous 10% solutions of copper sulphate, aqueous 10% silver nitrate and aqueous 10% lead nitrate, all containing wetting agent, for a period of greater than 2 hours. No stains of any colour were observed. Also, no stains were observed by wearing of gloves by hands, which had been contaminated with copper.

15

While in the foregoing specification this invention has been described in relation to certain preferred embodiments thereof, and many details have been set forth for purpose of illustration, it will be apparent to those skilled in the art, that the invention is susceptible to additional embodiments and that certain of the details



described herein can be varied considerably without departing from the basic principles of the invention.

**CLAIMS**

1. A process for preparing synthetic latex compound, the said process includes the steps of:
  - 5 a) adding a polyvalent metal chemical or a mixture thereof to a surfactant stabilised synthetic carboxylated latex, or blend with other synthetic latex to form a synthetic latex compound;
  - b) stirring the synthetic latex compound;
  - c) diluting the synthetic latex compound obtained in step (b) to a  
10 predetermined total solid content (TSC); and
  - d) maintaining the synthetic latex compound obtained in step (c) at a temperature between 0 to 80°C.
2. The process as claimed in claim 1, wherein the polyvalent metal chemical  
15 may be zinc oxide, zinc carbonate, calcium carbonate, magnesium oxide, magnesium carbonate, hydroxides of calcium, magnesium, aluminium or aluminates or any combinations thereof.
3. The process as claimed in claim 1, wherein the synthetic carboxylated latex  
20 may be a synthetic carboxylated butadiene co-polymer latex, a synthetic carboxylated acrylonitrile butadiene latex, a synthetic carboxylated styrene butadiene latex, a synthetic carboxylated chlorinated butadiene co-polymer latex or any blend of these latices.
- 25 4. The process as claimed in claim 1, wherein the synthetic carboxylated latex compound is synthetic carboxylated nitrile latex.

5. A synthetic latex compound obtained from a process which includes the steps of:

5 a) adding a polyvalent metal chemical or a mixture thereof to a surfactant stabilised synthetic carboxylated latex, or blend with other synthetic carboxylated or non-carboxylated latex or latices to form a synthetic latex compound;

b) stirring the synthetic latex compound;

10 c) diluting the synthetic latex compound obtained in step (b) to a predetermined total solid content (TSC); and

d) maintaining the synthetic latex compound obtained in step (c) at a temperature between 0 to 80°C.

15 6. The synthetic latex compound as claimed in claim 5, wherein the polyvalent metal chemical may be zinc oxide, zinc carbonate, calcium carbonate, magnesium oxide, magnesium carbonate, hydroxides of calcium, magnesium, aluminium or aluminates or any combinations thereof.

20 7. The synthetic latex compound as claimed in claim 5, wherein the synthetic latex compound is nitrile latex.

25 8. A non-staining rubber article such as a non-staining glove, condom, finger cot or balloon made from a composition containing an effective amount of synthetic carboxylated butadiene co-polymer latex and an effective amount of polyvalent metal chemical or mixture thereof as the sole cross-linking agent.

9. A non-staining rubber article such as a non-staining glove, condom, finger cot or balloon made from a composition containing an effective amount of synthetic polymer latex or latices, an effective amount of synthetic carboxylated butadiene co-polymer latex and an effective amount of polyvalent metal chemical as the sole cross-linking agent.
10. The non-staining rubber article as claimed in claim 8 or 9, wherein the rubber article is free from any sulphur and/or sulphur containing chemicals.
11. The non-staining rubber article as claimed in claim 8 or 9, wherein the synthetic carboxylated butadiene co-polymer latex is carboxylated acrylonitrile butadiene latex.
12. The non-staining rubber article as claimed in claim 8 or 9, wherein the polyvalent metal chemical are selected from any or a combination of oxides of zinc, magnesium, calcium or aluminium.
13. The non-staining rubber article as claimed in claim 12, wherein carbonates of zinc, magnesium, calcium or aluminium are combined with the oxides.
14. The non-staining rubber article as claimed in claims 8 and 9, wherein the zinc oxide level is equal to or greater than 0.6 phr.
15. The non-staining rubber article as claimed in claims 8 and 9, wherein the rubber article is free from rubber accelerators.

16. The non-staining rubber article as claimed in claims 8 and 9, wherein the rubber article is free from Type I and Type IV latex allergens.

- 5 17. The non-staining rubber article as claimed in claims 8 and 9, wherein the rubber article does not stain when in contact with skin or other surfaces, which are contaminated with copper, silver, iron or lead or chemicals of these metals.

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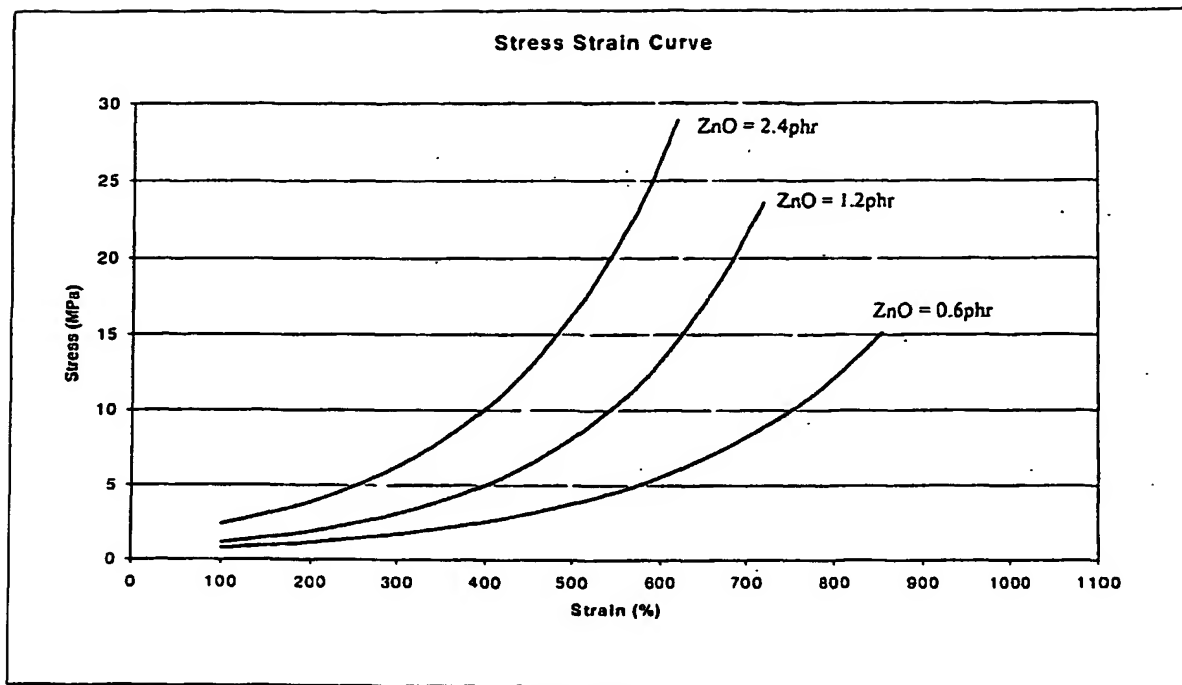


FIGURE 1

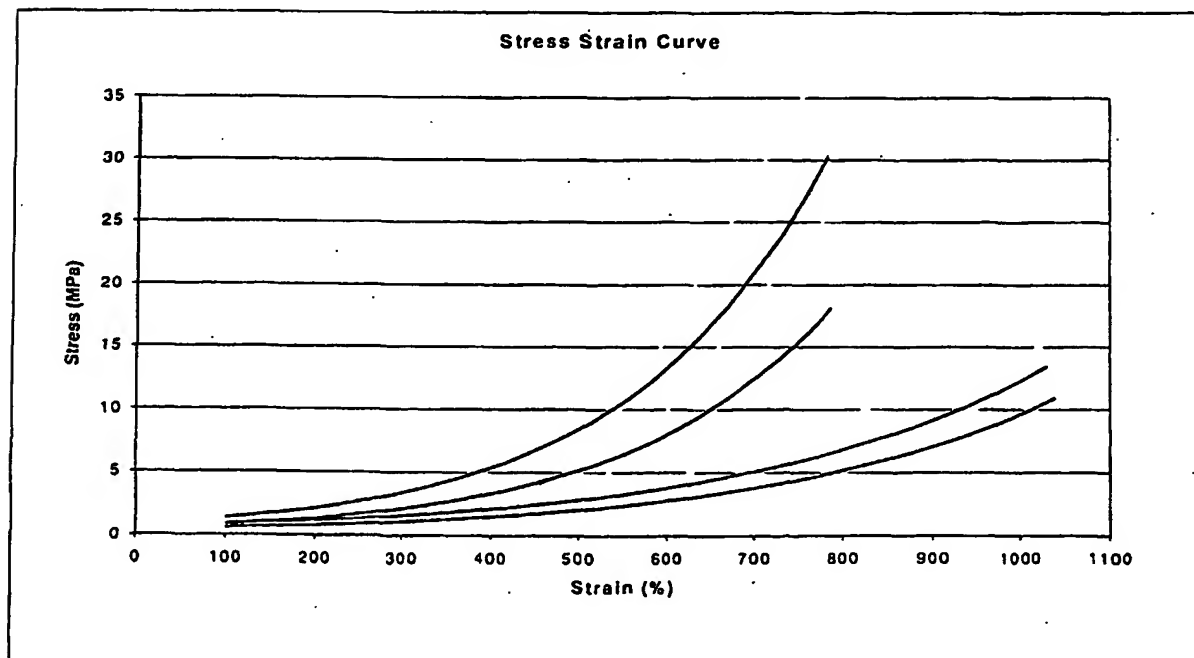


FIGURE 2

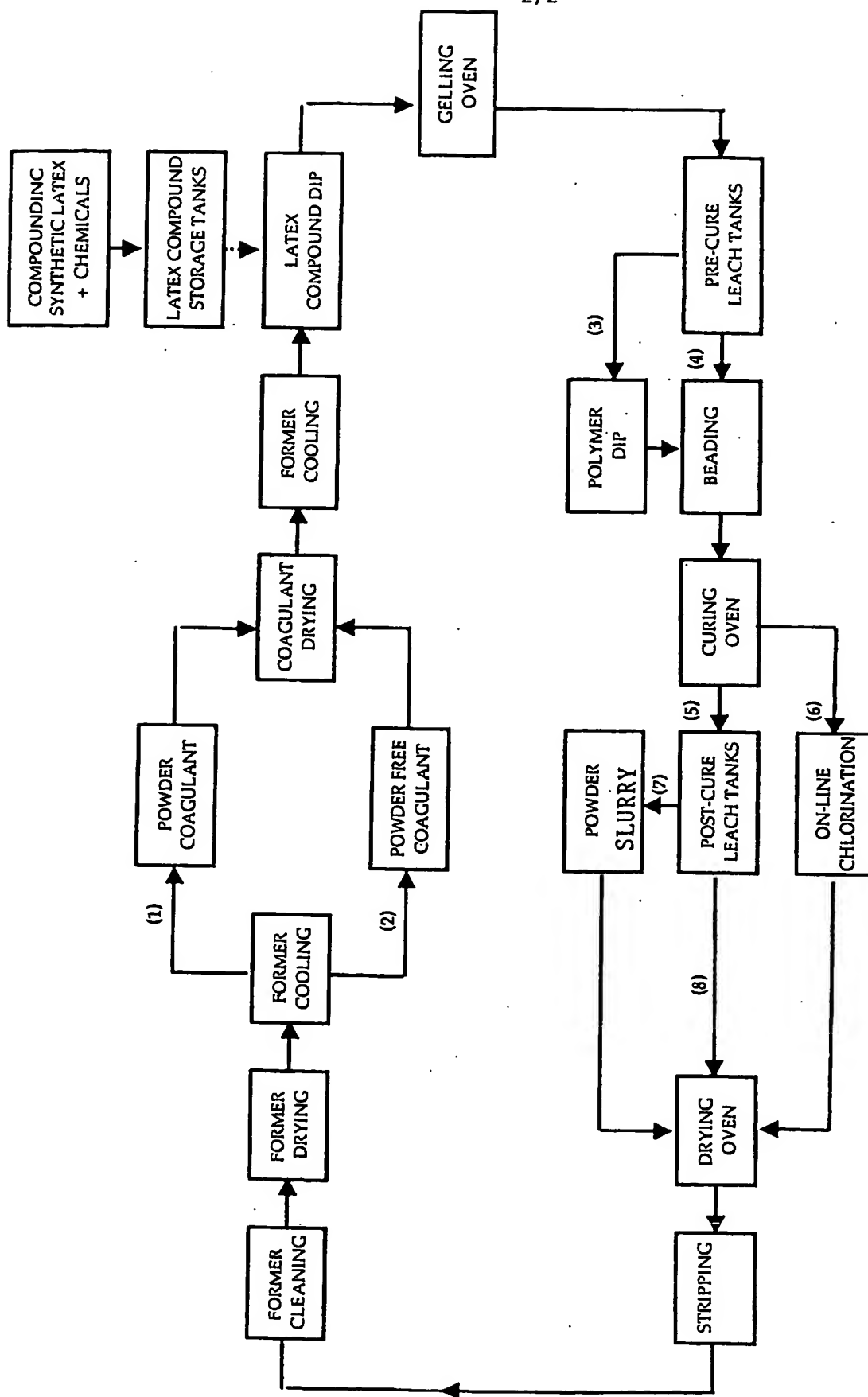


FIGURE 3

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/AU03/01350

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. <sup>7</sup>: C08J 3/26; C08F 8/42; C08C 19/26, 19/36; A61B 19/04; A41D 19/015; A61F 6/04; A63H 27/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPAT JAPIO USPTO

polyvalent metal, carboxylated, butadiene, nitrile, latex, crosslink, glove... and like terms.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/38640 A ( REICHHOLD, INC. ) 16 May 2002 Page 8, Example 1	1-17
X	WO 00/21451 A ( LRC PRODUCTS LIMITED ) 20 April 2000 Page 11	1-7
X	US 3931085 A ( Drelich et al. ) 6 January 1976 Example IX	1-7

☒ Further documents are listed in the continuation of Box C

☒ See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
5 November 2003

Date of mailing of the international search report  
13 NOV 2003

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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU03/01350

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/09590 A ( LRC PRODUCTS LTD. ) 24 February 2000 Example 1	8-17
X	US 5670263 A ( Gazeley ) 23 September 1997 Example 9	8-17
A	US 5747579 A ( Blakeman et al. ) 5 May 1998 Entire document	1-7
A	US 4952634 A ( Grossman ) 28 August 1990 Entire document	1-7
A	US 4394488 A ( Kim et al. ) 19 July 1983 Entire document	1-7
A	WO 02/50177 A ( KIMBERLY-CLARK WORLDWIDE, INC. ) 27 June 2002 Entire document	8-17
A	EP 456333 A ( TILLOTSON CORPORATION ) 13 November 1991 Entire document	8-17
A	US 5084514 A ( Szczechura et al. ) 28 January 1992 Entire document	8-17

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU03/01350

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
WO	0238640	AU	27257/02	EP	1355964	US	6624274
WO	0021451	AU	62234/99	CA	2346912	EP	1128776
		US	6566435				
US	3931085	AR	198840	AU	56678/73	CA	1003985
		DE	2329193	FR	2187828	GB	1430126
		IN	141141	IN	144616	JP	49066722
		NL	7307902	SE	7803939	US	3849173
		ZA	7303846				
WO	0009590	AU	53808/99	EP	1112304	US	2003075828
US	5670263	EP	0594410				
US	4952634	JP	1020264				
US	4394488	CA	1203049	FR	2511015	NL	8203135
WO	0250177	AU	31015/02	CA	2429840	EP	1358257
		US	2002114943				
EP	0456333	US	5014362				
US	5747579	AU	39675/89	EP	0350204	EP	0378668
		NZ	229722	WO	9000186	ZA	8904877
END OF ANNEX							